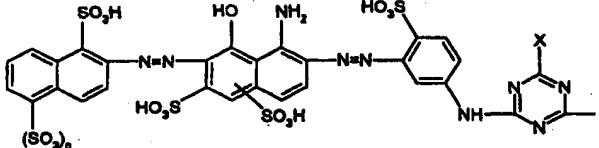
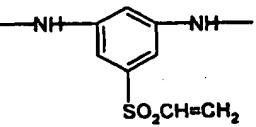


PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

BC

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :  C09B 62/09		A1	(11) International Publication Number: <b>WO 00/08104</b>  (43) International Publication Date: 17 February 2000 (17.02.00)		
(21) International Application Number: PCT/GB99/02447  (22) International Filing Date: 26 July 1999 (26.07.99)		(81) Designated States: BR, CN, IN, JP, KR, TR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).			
(30) Priority Data: 9816780.2 31 July 1998 (31.07.98) GB		Published <i>With international search report.</i>			
(71) Applicant (for all designated States except US): BASF AK-TIENGESELLSCHAFT [DE/DE]; D-67056 Ludwigshafen (DE).					
(72) Inventors; and (75) Inventors/Applicants (for US only): EBENEZER, Warren, James [GB/GB]; 28 Colwyn Road, Bramhall, Stockport SK7 2JQ (GB). MYNETT, Donna, Maria [GB/GB]; 44 Ashridge Avenue, Westbury Park, Newcastle-u-Lyme, Staffordshire ST6 4JA (GB).					
(74) Agents: COLEIRO, Raymond et al.; Mewburn Ellis, York House, 23 Kingsway, London WC2B 6HP (GB).					
(54) Title: REACTIVE DYES CONTAINING A LINKAGE					
 <p style="text-align: right;">(I)</p>					
<p style="text-align: center;"> <math>\begin{array}{c} R^1 \quad R^2 \\   \quad   \\ -Y- \text{ is } -N-Z-N- \quad (a) \quad \quad R^3 \\   \quad   \\ -N-Z-S-; \quad (b) \end{array}</math> </p>					
 <p style="text-align: center;">(c)</p>					
<p>(57) Abstract</p> <p>A reactive disazo dye has the formula (I) <math>D^1-Y-D^2</math> wherein each of <math>D^1</math> and <math>D^2</math> independently is a chromophore of formula (II) in which X is fluorine, chlorine or optionally substituted pyridinium; an <math>SO_3H</math> is present in the 5- or 6-position of the naphthalene nucleus; n is zero or 1; and <math>-Y-</math> is (a); or (b) in which: Z is a <math>C_{5-12}</math> aliphatic or aromatic cyclic hydrocarbon group, optionally additionally containing at least one hetero atom selected from N, O and S optionally substituted by at least one <math>C_{1-4}</math> alkyl and <math>SO_3H</math> (or a salt thereof); or at least two said cyclic hydrocarbon groups linked together, or a <math>C_{1-15}</math> alkylene or <math>C_{2-15}</math> alkenylene chain, which chain optionally additionally contains, and/or is substituted by, other atoms or groups; and each of <math>R^1</math>, <math>R^2</math> and <math>R^3</math>, independently, is a <math>C_{1-4}</math> alkyl, hydroxy-<math>C_{1-4}</math> alkyl or amino-<math>C_{1-4}</math> alkyl group or each of <math>R^1</math> and <math>R^2</math>, together with the respective nitrogen atoms to which they are attached and the chain Z therebetween, forms a heterocyclic group or one of <math>R^1</math>, <math>R^2</math> and <math>R^3</math>, together with (i) the nitrogen atom to which it is attached, (ii) the substituent group on the chain Z and (iii) the chain length between the said nitrogen atom and the said substituent group, forms a heterocyclic group; and Y is other than (c) or a sulphonate salt of the dye of the formula (I).</p>					

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NB	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

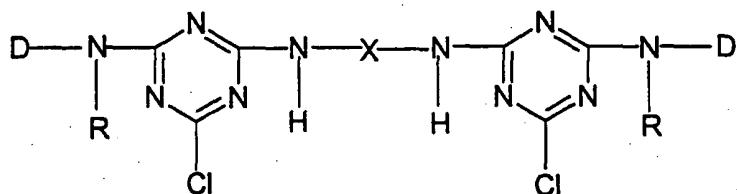
## REACTIVE DYES CONTAINING A LINKAGE

This invention relates to reactive dyes having a bridging group between triazinylamino groups each attached to a chromophore.

5

GB-A-1283771 and EP-A-0625551 disclose respective general ranges of reactive dyes of the formula (A)

10



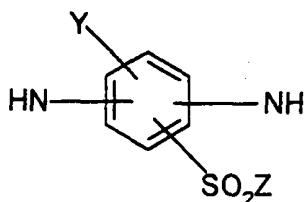
15

(A)

where D is a chromophore (which in the case of GB-A-1283771 is specifically a naphthylazo-phenylene or -naphthalene containing 20 at least 3 sulphonic acid groups and in the case of EP-A-0625551 is any of a wide range of chromophores), R is H or an optionally substituted C<sub>1-4</sub> alkyl group and X specifically a linking group which, in the case of GB-A-1283771, is an aromatic group selected from phenylene, diphenylene and naphthalene nuclei, and in the 25 case of EP-A-0625551 is an aliphatic linking group, the group -NHXNH- forming a bridging group between receptive triazine nuclei. The dyes of GB-A-1283771 offer a degree of fixation over a wide range of liquor to goods ratios and provide shades of very good light fastness, while those of EP-A-0625551 show good 30 fastness and build up properties.

JP-A-62-172062 discloses a wide range of dyestuffs in which chromophores are linked by the specific group

5



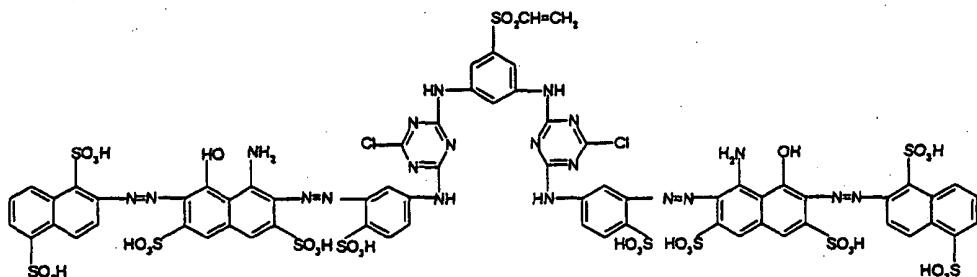
10

wherein Y is hydrogen, halogen or alkyl and Z is the reactive group  $-\text{CH}=\text{CH}_2$  or  $-\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$ .

15

One of many examples of dyes disclosed has the following formula

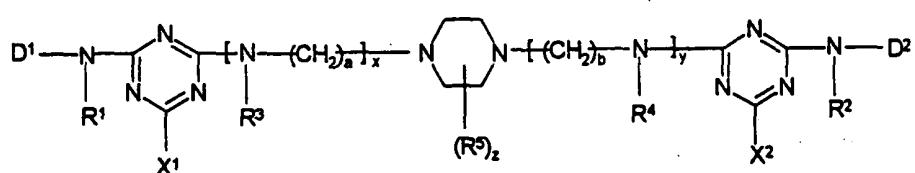
20



25

In our WO-A-99/05224, we describe a range of dyes in which the bridging group is derived from an aminoalkyl piperazine, which dyes have the formula (B)

30



(B)

35

wherein:

each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$ , independently, is H or an optionally substituted alkyl group;

each of  $X^1$  and  $X^2$ , independently, is a labile atom or group;

5 each of x and y, independently, is 0 or 1 and at least one of x and y is 1;

each of a and b, independently, is 2 to 5;

z is zero or is 1 to 4; and

when each of x and y is 1,  $a > b$ ;

10 the or each  $R^5$ , independently, is alkyl; and

each of  $D^1$  and  $D^2$ , independently, is a monoazo or polyazo chromophore, or a metallized derivative thereof.

We have found surprisingly that if, in dyes of the 15 above formula (A), the chromophore D is a particular disazo dye, defined below, then such dyes, especially when used for exhaust dyeing of cellulosic materials, can exhibit excellent all-round fastness properties and build-up and compatibility with other dyes whose preferred exhaust temperature is 80°C or, more 20 preferably, above.

Thus, according to one aspect, the invention provides a dye of the formula (I)

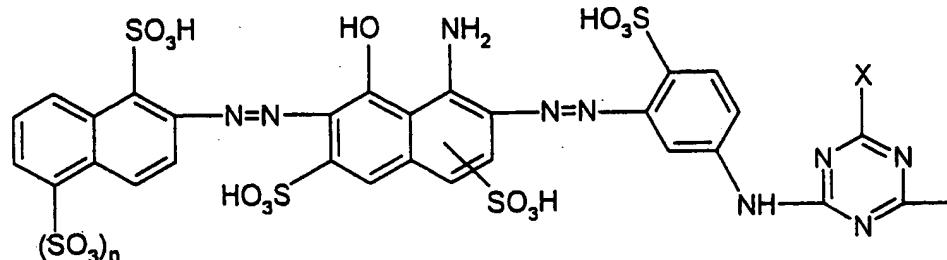
25



wherein each of  $D^1$  and  $D^2$  independently is a chromophore of the formula

30

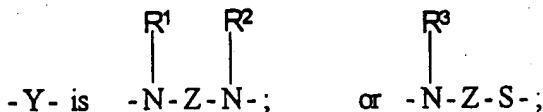
35



in which

X is fluorine, chlorine or optionally substituted pyridinium; an SO<sub>3</sub>H is present in the 5- or 6- position (preferably the 6- position) of the naphthalene nucleus;

5 n is zero or 1 (preferably 1); and



10 in which

Z is a C<sub>5-12</sub> aliphatic or aromatic cyclic hydrocarbon group, optionally additionally containing at least one hetero atom selected from N, O and S and optionally substituted by at least one of C<sub>1-4</sub> alkyl and SO<sub>3</sub>H (or a salt thereof); or

15 at least two said cyclic hydrocarbon groups linked together;

or

a C<sub>1-15</sub> alkylene or C<sub>2-15</sub> alkenylene chain, which said chain

(a) optionally additionally contains, so as to be interrupted or terminated by, at least one of (1) at least one 20 hetero atom selected from N, O and S and (2) at least one C<sub>5-12</sub> aliphatic or aromatic cyclic hydrocarbon group, which said cyclic hydrocarbon group optionally additionally contains at least one hetero atom selected from N, O and S and is optionally substituted by at least one of C<sub>1-4</sub> alkyl and SO<sub>3</sub>H (or a salt thereof); and

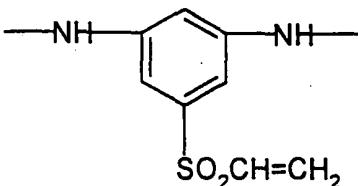
25 (b) is optionally substituted by C<sub>1-4</sub> alkyl, hydroxy-C<sub>1-4</sub> alkyl, amino-C<sub>1-4</sub> alkyl, hydroxyl, carboxyl or amino, which amino group or moiety is optionally substituted by one or two C<sub>1-4</sub> alkyl groups, or by a substituent group which, together with (i) one of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> (each defined below), (ii) the nitrogen atom to which R<sup>1</sup>, R<sup>2</sup> or R<sup>3</sup> is attached and (iii) a chain length of Z between the said nitrogen and the substituent group, forms a heterocyclic group; and

30 each of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>, independently, is a C<sub>1-4</sub> alkyl, hydroxy-C<sub>1-4</sub> alkyl or amino-C<sub>1-4</sub> alkyl group or each of R<sup>1</sup> and R<sup>2</sup>, together

with the respective nitrogen atoms to which they are attached and the chain Z therebetween, forms a heterocyclic group or (as defined above) one of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>, together with (i) the nitrogen atom to which it is attached, (ii) the said substituent group on the chain Z and (iii) the said chain length between the said nitrogen atom and the said substituent group, forms a heterocyclic group; and

Y is other than

10



15 (and preferably contains no reactive group); or a sulphonic acid salt of the said dye of the formula (I).

When X is a substituted pyridinium, preferred substituents are 3-carboxyl, 3-carbonamido and 4-carboxyl.

20

In one preferred range of dyes, Z is a C<sub>1-10</sub> alkylene chain optionally substituted by at least one group selected from C<sub>1-4</sub> alkyl, hydroxy and carboxyl. Such chains may be free from any hetero atom or may contain additionally at least one hetero atom 25 selected from O and N. More preferably, the chain is a C<sub>2-8</sub>-alkylene chain which is unsubstituted or substituted by at least one group selected from methyl, hydroxy and carboxyl. Still more preferably the chain is of the formula

30



wherein x is 2 or 3, which alkylene chain is unsubstituted or substituted by one or two methyl groups or a hydroxy or carboxyl group and each of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently is selected from 35 hydrogen, C<sub>1-4</sub> alkyl and hydroxyethyl.

Examples of the group Y in which Z is a  $C_{1-10}$  alkylene chain optionally substituted by at least one of  $C_{1-4}$  alkyl, hydroxy and carboxyl are  $HNC_2H_4NH$ ;  $HNC_3H_6NH$ ;  $HNC_4H_8NH$ ;  $HNC_5H_{10}NH$ ;  $HNC_6H_{12}NH$ ;  $HNC_8H_{16}NH$ ;  $HNC_2H_4N(CH_3)$ ;  $HNC_3H_6N(CH_3)$ ;  $HNC_2H_4N(C_2H_4OH)$ ;  $HNC_2H_4N(C_3H_6OH)$ ;

5  $HNC_3H_6N(C_2H_4OH)$ ;  $HNC_2H_4N(C_2H_5)$ ;  $HNC_2H_4N(n-C_3H_7)$ ;  $HNC_3H_6N(C_2H_5)$ ;

$HNC_3H_6N(n-C_3H_7)$ ;  $(H_3C)NC_2H_4N(CH_3)$ ;  $(H_3C)NC_3H_6N(CH_3)$ ;  $(H_3C)NC_2H_4N(C_2H_5)$ ;

$HNC_2H_4NH[CH(CH_3)_2]$ ;  $(H_5C_2)NC_2H_4N(C_2H_5)$ ;  $HNC_2H_4NH[CH(CH_3)(C_2H_5)]$ ;

$HNC_2H_4N(n-C_4H_9)$ ;  $HNC_2H_4N[CH_2CH(CH_3)(OH)]$ ;  $HNCH(CH_3)CH_2NH$ ;

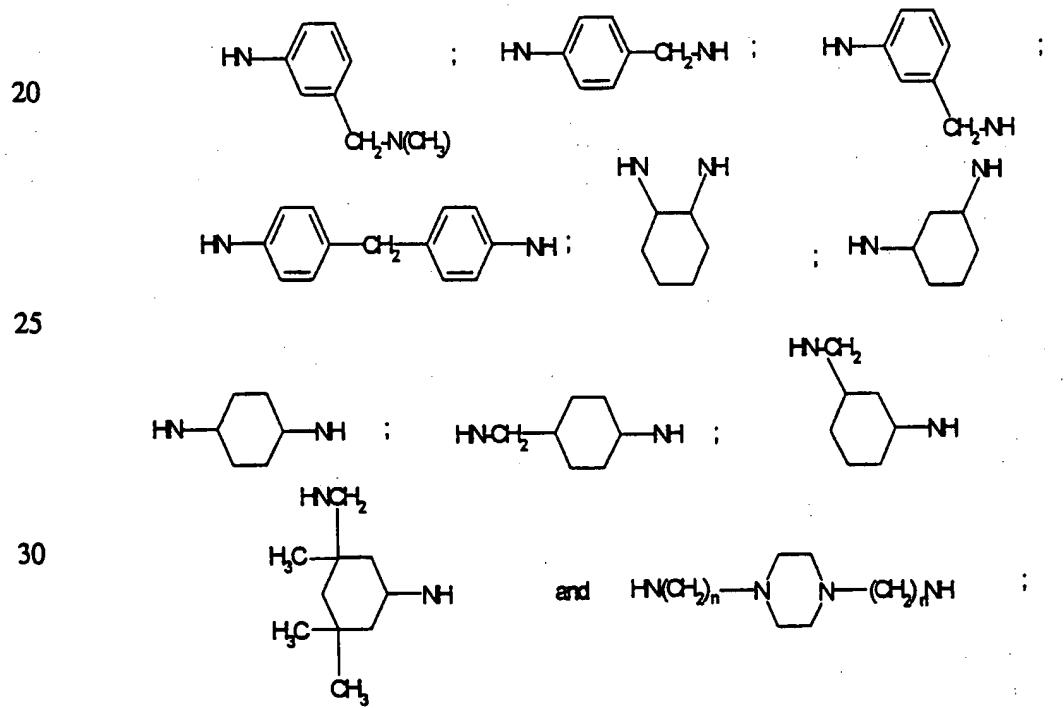
10  $HNC(CH_3)_2CH_2NH$ ;  $HNCH_2CH(OH)CH_2NH$ ;  $HNCH_2C(CH_3)_2CH_2NH$ ;  $HNCH(C_2H_5)CH_2NH$ ;

$HNCH_2CH(CH_3)C_3H_6NH$ ;  $HNCH_2CH(CH_3)N[CH(CH_3)_2]$ ;  $NHCH_2C(CH_3)_2CH[CH(CH_3)_2]NH$ ;

$HNC_2H_4S$  and  $HNCH(CO_2H)CH_2S$ .

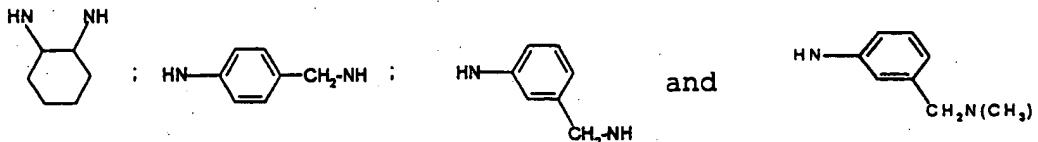
Examples of the group Y in which Z is a  $C_{1-10}$  alkylene chain additionally containing a hetero atom are  $HNC_3H_6N(CH_3)C_3H_6NH$ ;  $HNC_2H_4OC_2H_4OC_2H_4NH$ ; and  $HNC_2H_4OC_2H_4NH$ .

15 The  $C_{1-10}$  alkylene chain of Z may additionally contain an aliphatic or aromatic ring structure and examples of the group Y in which Z is such a chain are:



where n is 2 or 3, which is an example of the group Y in which Z is  $C_{1-10}$  alkylene chain interrupted by an aliphatic ring containing at least one hetero atom. Of these groups,

5

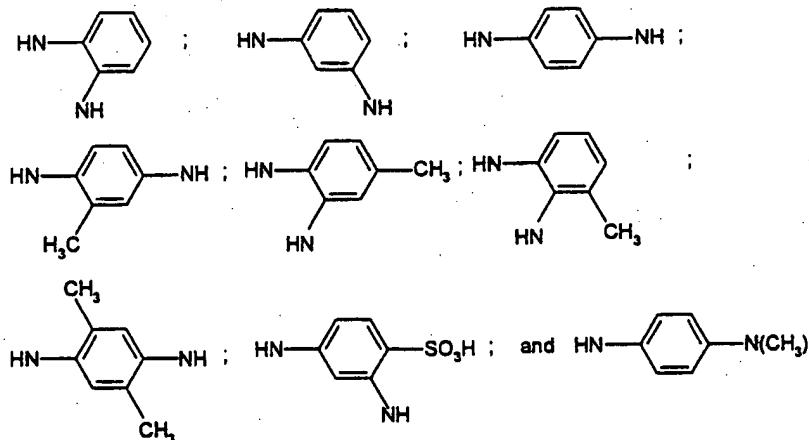


are especially preferred.

Especially preferred examples of the group Y in which Z is a  $C_{1-10}$  alkylene chain are  $NHC_2H_4NH$ ;  $NHC_3H_6NH$ ;  $NHCH(CH_3)CH_2NH$ ;  $NHC_2H_4N(CH_3)$ ;  $NHC_3H_6N(CH_3)$ ;  $NHCH_2CH(OH)CH_2NH$ ;  $NHC_2H_4N(C_2H_4OH)$ ;  $NHC(CH_3)_2CH_2NH$ ;  $NHC_3H_6N(C_2H_4OH)$ ;  $NHC_2H_4S$ ;  $NHC_2H_4N(C_2H_5)$ ;  $N(CH_3)C_2H_4N(CH_3)$ ;  $NHC_3H_6N(C_3H_7)$ ;  $N(C_2H_4OH)C_2H_4N(C_2H_4OH)$ ;  $HNCH(CO_2H)CH_2S$ ;  $N[CH(CH_3)_2]CH(CH_3)CH_2NH$ ;  $HNC_6H_{12}NH$ ;  $HNC_3H_6N(CH_3)C_3H_6NH$ ;  $HNC_2H_4OC_2H_4NH$ ; and  $HNC_2H_4OC_2H_4OC_2H_4NH$ .

In another preferred range of dyes, Z is a phenylene group, optionally substituted by a sulphonic acid group or one or more methyl group(s). Examples of the group Y in which Z is a phenylene group are:

25



30

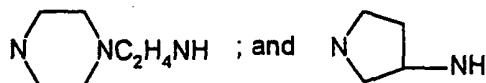
or mixtures thereof, for example, a mixture of

5



In yet another preferred range of dyes Z is a C<sub>1-15</sub> alkylene chain and is substituted by a substituent group, preferably a C<sub>1-10</sub> alkylene group, which, together with (i) one of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>, (ii) the nitrogen atom to which R<sup>1</sup>, R<sup>2</sup> or R<sup>3</sup> is attached and (iii) a chain length of Z between the said nitrogen atom and the substituent group, forms a heterocyclic group. More preferably, the C<sub>1-15</sub> alkylene chain is interrupted by a nitrogen atom which 10 carries the substituent group, for example, in the case where Y is an imino-C<sub>1-14</sub> alkylpiperazinyl group. Examples of Y in which the 15 group Z includes a heterocyclic ring formed in this manner are:

20

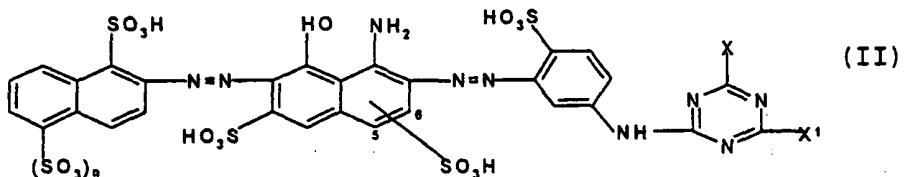


In another preferred range of dyes, each of R<sup>1</sup> and R<sup>2</sup>, together with the respective nitrogen atoms to which they are attached and the chain Z therebetween, form a heterocyclic group, more preferably a piperazine group.

25

A dye of the formula (I), given and defined above, can be prepared by a method aspect of the invention, which method comprises allowing at least one reactive disazo dye of the formula (II)

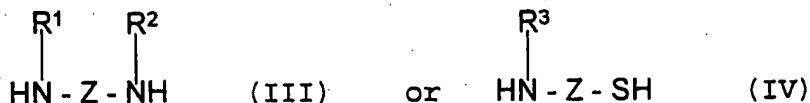
30



35

wherein X and n are as defined above and X<sup>1</sup> is a fluorine, chlorine or optionally substituted pyridinium group, to react with a diamine or thioamine of the formula

5

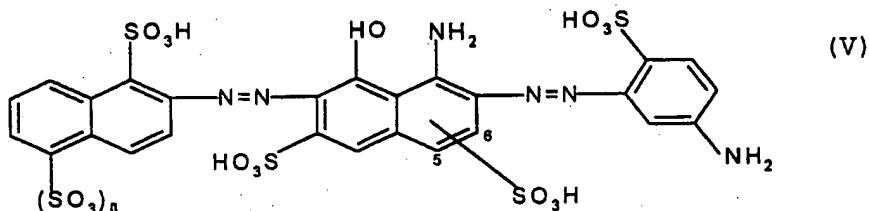


wherein each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and Z is as defined above, at a pH of from 7 to 10, in a proportional amount of two moles of reactive 10 disazo dye (II) per mole of diamine or thioamine (III) or (IV). The reaction may take from 1 - 12 hours.

The reactive disazo dye of the above formula (II) can be prepared by reacting a disazo dye of the formula (V)

15

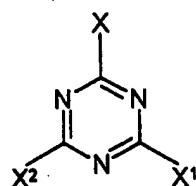
20



25

with a triazine of the formula

30



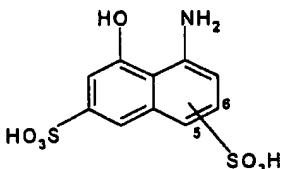
wherein each of X, X<sup>1</sup> and X<sup>2</sup> independently is chlorine, fluorine or optionally substituted pyridinium.

35

10

The disazo dye of the formula (V) may be prepared by firstly diazotising 4-acetylaminobenzene sulphonic acid and coupling in acid conditions (pH of 2) onto a hydroxynaphthylamine of the formula

5



10

and secondly diazotising 2-aminonaphthalene-1,5-disulphonic acid 15 and coupling in neutral conditions (pH of 7) onto the hydroxynaphthylamine. Thereafter, removal of the acetyl protecting group of the amino group meta to the azo linkage yields the disazo dye of the formula (V).

Although dye formulae have been shown in the form of their 20 free acid in this specification, the invention also includes dyes and processes using dyes in the salt form, particularly their salts with alkali metals such as the potassium, sodium, lithium or mixed sodium/lithium salt.

The dyes may be used for dyeing, printing or ink- 25 jet printing, for example, of textile materials and paper.

The process for colouration is preferably performed at a pH of 7.1 to 13, more preferably 10 to 12. pH levels above 7 can be achieved by performing the process for colouration in the presence of an acid-binding agent.

30

The substrate may be any of a textile material, leather, paper, hair or film, but is preferably a natural or artificial textile material containing amino or hydroxyl groups, for example textile material such as wool, silk, polyamides and modified 35 polyacrylonitrile fibres, and more preferably a cellulosic textile

material, especially cotton, viscose and regenerated cellulose, for example, that commercially available as Tencel. For this purpose the dyes can be applied to the textile materials at a pH above 7 by, for example, exhaust dyeing, padding or printing. Textile 5 materials are coloured bright shades and possess good fastness to light and wet treatments such as washing.

The new dyes are particularly valuable for colouring cellulosic textile materials. For this purpose, the dyes are 10 preferably applied to the cellulosic textile material at a pH above 7 in conjunction with a treatment with an acid-binding agent.

Preferred acid-binding agents include alkali metal carbonates, bicarbonates, hydroxides, metasilicates and mixtures thereof, for 15 example, sodium bicarbonate, sodium carbonate, sodium metasilicate, sodium hydroxide and the corresponding potassium salts. The dyes benefit from excellent build-up and high fixation.

At least for cellulosic materials, dyeing may be carried out 20 at a temperature of from 80 to 105°C, preferably 85 to 95°C, still more preferably at about 90°C, a somewhat higher temperature as compared with dyeing carried out with conventional monochlorotriazine exhaust dyes which are generally dyed at temperatures of about 80°C. By operating at this temperature, 25 particularly improved migration is obtained.

The new dyes can be applied to textile materials containing amine groups, such as wool and polyamide textile materials, from a neutral to mildly alkaline dyebath. The dyeing process can be 30 carried out at a constant or substantially constant pH, that is to say the pH of the dyebath remains constant or substantially constant during the dyeing process, or if desired the pH of the dyebath can be altered at any stage of the dyeing process.

The dyes may be in liquid or solid form, for example in granular or powdered form.

We find surprisingly that such dyes provide the following advantageous properties:

- 5 a) good all-round fastness;
- b) exceptionally good build-up, especially at a dyeing temperature of 90°C;
- c) very strong dyeing;
- d) exceptionally good robustness to changes in dyeing
- 10 conditions, especially temperature, pH and, in particular, dyebath liquor to substrate ratio, leading to overall excellent shade reproducibility;
- e) good wash off;
- f) good fixation;
- 15 g) good aqueous solubility; and
- h) good compatibility with other dyes of this type.

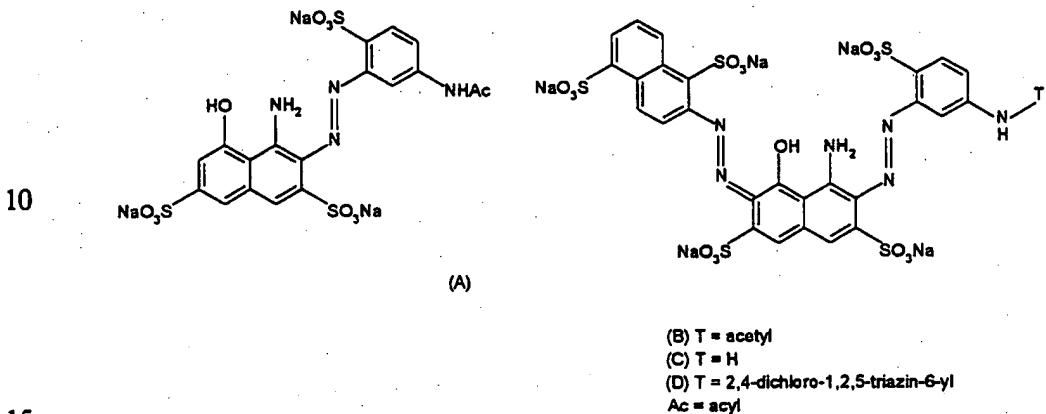
Especially preferred embodiments of the invention will now be described in more detail with reference to the following Examples 20 in which all parts and percentages are by weight unless otherwise stated. Although preparation and dyeing with any single dye is exemplified, particular advantages can be seen when dyeing with mixtures of dyes.

25 Example 1

An aqueous solution of sodium 4-acetylamino-2-aminobenzenesulphonate (0.75 mole) and sodium nitrite (390 ml 2N) was added to stirred ice (1 kg) containing concentrated hydrochloric acid (150 ml) over 30 minutes maintaining the 30 temperature below 5°C. Excess nitrite was decomposed with 10% sulphamic acid solution. An aqueous solution of the sodium salt of H-acid (0.5 mole in 600 ml) was added slowly to the well-stirred diazonium salt solution over 45 mins below 5°C at pH 2. The mixture was stirred below 5°C for 2 h, and then allowed to warm to

room temperature overnight. The intermediate (A) was screened off and dried to a damp paste at 40°C.

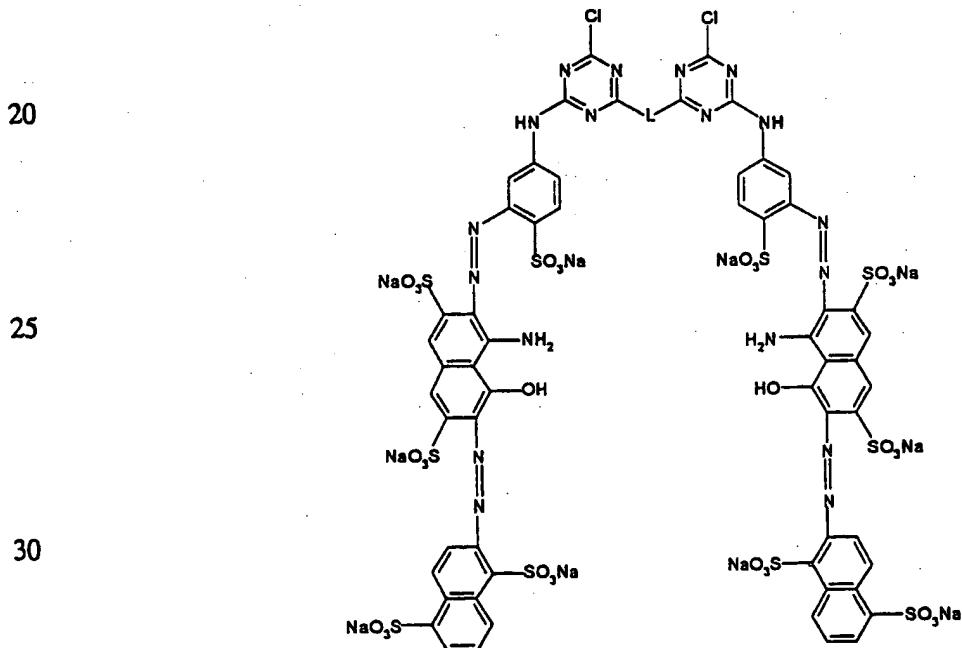
5



15

An aqueous solution of sodium 2-aminonaphthalene-1,5-disulphonate (0.12 mole in 200 ml water) and sodium nitrite (60 ml 2N) was added to stirred ice (200g) containing concentrated hydrochloric acid (30 ml) over 30 minutes maintaining the temperature below 5°C. Stirring was continued for a further 30 mins when excess nitrite was decomposed with 10% sulphamic acid solution. Intermediate (A) (ca 0.1mole) in water (800 ml) was treated with sufficient concentrated NaOH solution to ensure solution and cooled to below 5°C. This was added in a steady stream to the diazonium solution below 5°C whilst the pH gradually rose to 4 when coupling commenced. After 2 h at pH 4 below 5°C the pH was raised to 7 and the solution stirred overnight whilst warming to room temperature. The solution was filtered, the filtrate concentrated, and treated with methylated spirit to precipitate intermediate (B). This could be purified by redissolving in water and re-precipitating.

The protecting acetyl group was removed from intermediate (B) (0.1 mole) by hydrolysis with KOH (112g) in aqueous solution at 55°C for 2.5h. The alkaline solution was neutralised with hydrochloric acid and concentrated to give successive crops of 5 deacetylated intermediate (C). This (0.0262 mole) was dissolved in water (600 ml) and cooled to below 5°C and then treated with excess cyanuric chloride (5.08g; 0.0275 mole) dissolved in acetone. The well-stirred mixture was maintained at pH 6-6.5 for 2h, after which insolubles were filtered off. The filtrate (containing 0.0131 mole 10 dye (D)) was stirred with ethylenediamine (0.4g; 0.00655 mole) overnight at pH 10. The pH was then adjusted to 7 and the reaction mixture concentrated. Addition of methylated spirit precipitated the product (1; below) as a blue powder, which could be purified by 15 dialysis. As can be seen from Table 1, this had  $\lambda_{\max} = 616\text{nm}$ ,  $\epsilon_{\max} = 86500$ , 1/2-band width (HBW) = 117nm, and dyed cotton a greenish-navy shade with excellent all-round fastness properties.



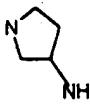
(i)  $L = NHC_2H_4NH$

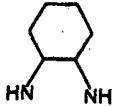
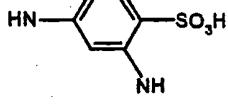
## Examples 2-30

By replacing the ethylenediamine of Example 1 by an alternative diamine or mercaptoalkylamine,  $LH_2$ , analogues of (1) 5 differing in the nature of the linking group, L, have also been prepared, as listed in Table 1.

Table 1

10	Example number	L in structure (1)	Shade on cotton	$\lambda_{\max}$ nm	$\epsilon_{\max}$	HBW nm
11	1	$NHC_2H_4NH$	greenish navy	616	86,500	117
12	2	1,3- $NHC_6H_4NH$	greenish navy	616	83,200	123
13	3		greenish navy	613	91,000	117
14	4	$NHC_3H_6NH$	greenish navy	617	91,100	116
15	5	$NHCH(Me)CH_2NH$	greenish navy	615	88,900	114
16	6	$NHC_2H_4N(Me)$	greenish navy	616	82,700	117
17	7	$NHC_3H_6N(Me)$	greenish navy	616	100,200	112
18	8	$NHCH_2CH(OH)CH_2NH$	greenish navy	616	91,500	114
19	9	1,4- $NHC_6H_4N(Me)$	greenish navy			

10	1, 4-NHC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NH	greenish navy	616	88,200	109
11		greenish navy	616	83,900	117
5	12 NHC <sub>2</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>4</sub> OH)	greenish navy	616	89,900	116
10	13 NHC(Me) <sub>2</sub> CH <sub>2</sub> NH	greenish navy			
15	14 NHC <sub>3</sub> H <sub>6</sub> N(C <sub>2</sub> H <sub>4</sub> OH)	greenish navy	616	89,600	113
16	15 NHC <sub>2</sub> H <sub>4</sub> S	greenish navy	615	90,100	123
17	16 1, 3-NHC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> N(Me)	greenish navy			
18	17 NHC <sub>6</sub> H <sub>12</sub> NH	greenish navy			
19	18 NHC <sub>2</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> )	greenish navy			
20	19 NHC <sub>3</sub> H <sub>6</sub> N(Me)C <sub>3</sub> H <sub>6</sub> NH	greenish navy	622	108,400	110
	20 	greenish navy			

21	1, 4-NHC <sub>6</sub> H <sub>4</sub> NH	greenish navy			
22	N(Me)C <sub>2</sub> H <sub>4</sub> N(Me)	greenish navy			
5	23 NHC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> NH	greenish navy			
24		greenish navy			
10	25 NHC <sub>3</sub> H <sub>6</sub> N(C <sub>3</sub> H <sub>7</sub> )	greenish navy			
26	N(C <sub>2</sub> H <sub>4</sub> OH)C <sub>2</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>4</sub> OH)	greenish navy			
15	27 NHC <sub>2</sub> H <sub>4</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> NH	greenish navy			
28		greenish navy			
29	HNCH(CO <sub>2</sub> H)CH <sub>2</sub> S	greenish navy			
30	N(i-Pr)CH(Me)CH <sub>2</sub> NH	greenish navy			
20	31 (Et)NC <sub>2</sub> H <sub>4</sub> N(Me)	greenish navy	616	104,700	113
32	HNC <sub>2</sub> H <sub>4</sub> N(C <sub>3</sub> H <sub>7</sub> )	greenish navy	616	99,900	113

## Examples 33 - 62

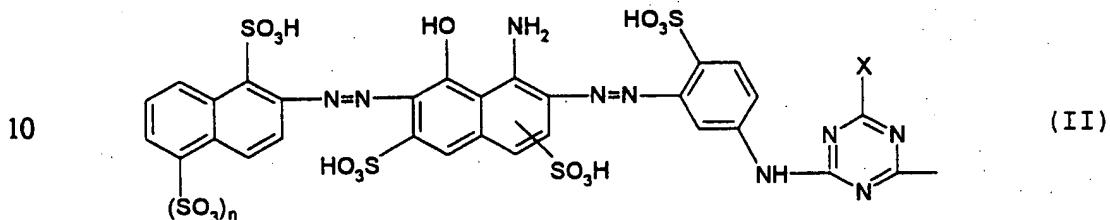
Each of the dyes prepared in Examples 1-32 was applied to cotton by exhaust dyeing at 90°C at a liquor : goods ratio of 10:1 and in the presence of salt and soda ash. In each case, the dye was found to have excellent build-up, extremely high fixation efficiency and good all round fastness properties.

## CLAIMS:

1. A dye of the formula (I)

wherein each of  $D^1$  and  $D^2$  independently is a chromophore of the

5 formula (II)

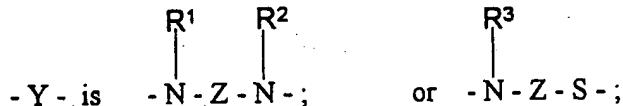


15 in which  $X$  is fluorine, chlorine or optionally substituted  
pyridinium;

an  $SO_3H$  is present in the 5- or 6- position of the naphthalene  
nucleus;

n is zero or 1; and

20



in which:

Z is a  $C_{5-12}$  aliphatic or aromatic cyclic hydrocarbon group,  
optionally additionally containing at least one hetero atom  
selected from N, O and S and optionally substituted by at least one  
of  $C_{1-4}$  alkyl and  $SO_3H$  (or a salt thereof); or

at least two said cyclic hydrocarbon groups linked together;  
or

a  $C_{1-15}$  alkylene or  $C_{2-15}$  alkenylene chain, which said chain

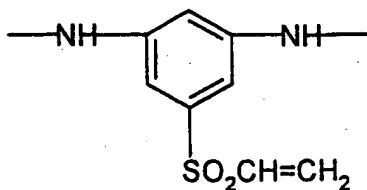
5 (a) optionally additionally contains, so as to be interrupted  
or terminated by, at least one of (1) at least one hetero atom  
selected from N, O and S and (2) at least one  $C_{5-12}$  aliphatic or

aromatic cyclic hydrocarbon group, which said cyclic hydrocarbon group (2) optionally additionally contains at least one hetero atom selected from N, O and S and is optionally substituted by at least one of C<sub>1-4</sub> alkyl and SO<sub>3</sub>H (or a salt thereof); and

5 (b) is optionally substituted by C<sub>1-4</sub> alkyl, hydroxy-C<sub>1-4</sub> alkyl, amino-C<sub>1-4</sub> alkyl, hydroxyl, carboxyl or amino, which amino group or moiety is optionally substituted by one or two C<sub>1-4</sub> alkyl groups, or by a substituent group which, together with (i) one of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> (each defined below), (ii) the nitrogen atom to which R<sup>1</sup>, R<sup>2</sup> or R<sup>3</sup> is attached and (iii) a chain length of Z between the said nitrogen atom and the substituent group, forms a heterocyclic group; and

10 15 each of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>, independently, is a C<sub>1-4</sub> alkyl, hydroxy-C<sub>1-4</sub> alkyl or amino-C<sub>1-4</sub> alkyl group or each of R<sup>1</sup> and R<sup>2</sup>, together with the respective nitrogen atoms to which they are attached and the chain Z therebetween, forms a heterocyclic group or (as defined above) one of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>, together with (i) the nitrogen atom to which it is attached, (ii) the said substituent group on the chain Z and (iii) the said chain length between the said nitrogen atom and the said substituent group, forms a heterocyclic group; and

20 Y is other than



30 or a sulphonic acid salt of the said dye of the formula (I).

2. A dye according to claim 1, wherein Z is non-reactive.

3. A dye according to claim 1 or claim 2, wherein n is 1.

4. A dye according to any preceding claim, wherein the group SO<sub>3</sub>H attached to the amino-bearing ring of the naphthalene nucleus is substituted in the 6-position thereof.

35

5. A dye according to any preceding claim, wherein Z is a C<sub>1-10</sub> alkylene chain optionally substituted by at least one group selected from C<sub>1-4</sub> alkyl, hydroxy and carboxyl groups.

6. A dye according to claim 5, wherein the C<sub>1-10</sub> alkylene chain is free from any hetero atom.

7. A dye according to claim 6, wherein the alkylene chain is a C<sub>2-8</sub> alkylene chain which is unsubstituted or substituted by at least one group selected from methyl, hydroxy and carboxyl.

8. A dye according to claim 7, wherein the alkylene chain is [CH<sub>2</sub>]<sub>x</sub>, wherein x is 2 or 3, which alkylene chain is unsubstituted or substituted by one or two methyl groups or hydroxy or carboxyl groups and each of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently is selected from hydrogen, C<sub>1-4</sub> alkyl and hydroxyethyl.

9. A dye according to claim 8, wherein Y is selected from NHC<sub>2</sub>H<sub>4</sub>NH; NHC<sub>3</sub>H<sub>6</sub>NH; NHCH(CH<sub>3</sub>)CH<sub>2</sub>NH; NHC<sub>2</sub>H<sub>4</sub>N(CH<sub>3</sub>); NHC<sub>3</sub>H<sub>6</sub>N(CH<sub>3</sub>); NHCH<sub>2</sub>CH(OH)CH<sub>2</sub>NH; NHC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH); NHC(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>NH; NHC<sub>3</sub>H<sub>6</sub>N(C<sub>2</sub>H<sub>4</sub>OH); NHC<sub>2</sub>H<sub>4</sub>S; NHC<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>5</sub>); N(CH<sub>3</sub>)C<sub>2</sub>H<sub>4</sub>N(CH<sub>3</sub>); NHC<sub>3</sub>H<sub>6</sub>N(C<sub>3</sub>H<sub>7</sub>); N(C<sub>2</sub>H<sub>4</sub>OH)C<sub>2</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>4</sub>OH); HNCH(CO<sub>2</sub>H)CH<sub>2</sub>S and N[CH(CH<sub>3</sub>)<sub>2</sub>]CH(CH<sub>3</sub>)CH<sub>2</sub>NH.

10. A dye according to claim 7, wherein Y is NHC<sub>6</sub>H<sub>12</sub>NH.

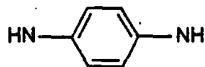
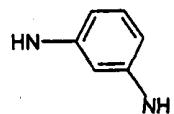
11. A dye according to claim 5, wherein the C<sub>1-10</sub> alkylene chain additionally contains at least one hetero atom selected from O and N.

12. A dye according to claim 11, wherein Y is selected from NHC<sub>3</sub>H<sub>6</sub>N(CH<sub>3</sub>)C<sub>3</sub>H<sub>6</sub>NH, NCH<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>NH and NHC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>NH.

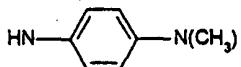
13. A dye according to any one of claims 1 to 4, wherein Z is a phenylene group, which phenylene group is unsubstituted or substituted by a sulphonic acid group and one or more methyl group(s).

21

14. A dye according to claim 13, wherein Y is selected from:



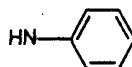
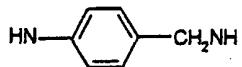
; and



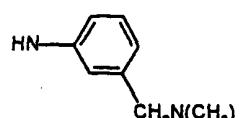
15. A dye according to claim 3, wherein the C<sub>1-10</sub> alkylene chain additionally contains at least one phenylene group.

16. A dye according to claim 15, wherein Y is selected from:

10

CH<sub>2</sub>N(CH<sub>3</sub>)

; and



15

17. A dye according to any one of claims 1 to 4, wherein Z is a C<sub>1-15</sub> alkylene chain and is substituted by a substituent group which, together with (i) one of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>, (ii) the nitrogen atom to which R<sup>1</sup>, R<sup>2</sup> or R<sup>3</sup> is attached and (iii) a chain length of Z between the said nitrogen atom and the substituent group, forms a heterocyclic group.

20

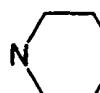
18. A dye according to claim 17, wherein the C<sub>1-15</sub> alkylene chain is interrupted by a nitrogen atom, which nitrogen atom carries the substituent group.

25

19. A dye according to claim 18, wherein Y is an imino-C<sub>1-4</sub> alkylpiperazinyl group.

30

20. A dye according to claim 17, wherein Y is selected from:



NC<sub>2</sub>H<sub>4</sub>NH ; and

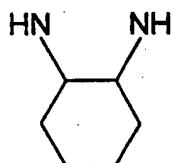


35

21. A dye according to any one of claims 1 to 4, wherein Z is an aliphatic cyclic hydrocarbon.

22. A dye according to claim 21, wherein Y is

5



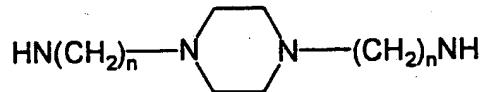
10

23. A dye according to any one of claims 1 to 4, wherein Z is a C<sub>1-15</sub> alkylene chain containing an aliphatic or aromatic cyclic hydrocarbon group, which group contains at least one hetero atom.

15

24. A dye according to claim 23, wherein Y is

20

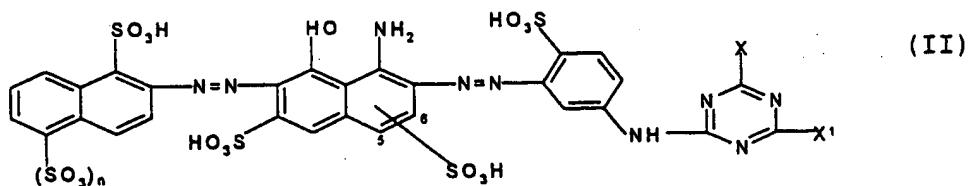


wherein n is 2 or 3.

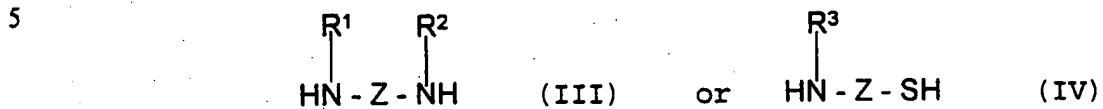
25

25. A method of preparing a dye of the formula (I), given and defined in claim 1, which method comprises allowing at least one reactive disazo dye of the formula (II)

30

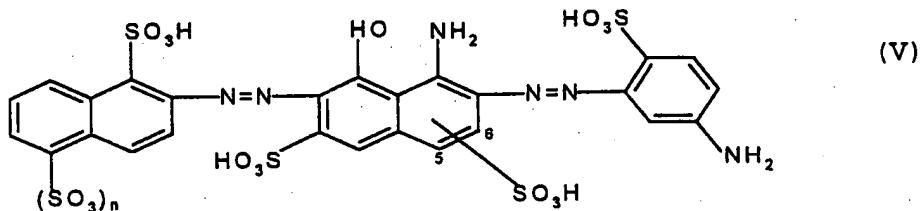


wherein X and n are as defined in claim 1 and X<sup>1</sup> is a fluorine, chlorine or optionally substituted pyridinium group, to react with a diamine or thioamine of the formula

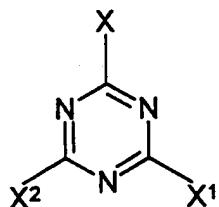


10 wherein each of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> and Z is as defined in claim 1, at a pH of from 7 to 10, in a proportional amount of two moles of reactive disazo dye (II) per mole of diamine or thioamine (III) or (IV).

15 26. A method according to claim 25, which includes the preliminary step of preparing the reactive disazo dye of the formula (II) by reacting a disazo dye of the formula (V)



wherein n is zero or 1, with a triazine of the formula



30 wherein each of X, X<sup>1</sup> and X<sup>2</sup> independently is chlorine, fluorine or optionally substituted pyridinium.

27. A process for the colouration of a substrate, which process comprises applying to the substrate, at a pH above 7, a dye according to any one of claims 1 to 24.
28. A process according to claim 27, wherein the dye is applied to 5 the substrate by exhaust dyeing, padding or printing.
29. A process according to claim 28, wherein the dye is applied to the substrate by exhaust dyeing at a temperature of from 80 to 105°C.
30. A process according to claim 29, wherein the exhaust dyeing is 10 carried out at a temperature of 85°C to 95°C.

# INTERNATIONAL SEARCH REPORT

Int'l. Application No

PCT/GB 99/02447

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C09B62/09

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 18224 A (CIBA GEIGY AG) 16 September 1993 (1993-09-16)	1-10
Y	page 48, paragraph 1 - paragraph 3; examples 99,100 page 20, paragraph 3 -page 21, line 2	1-30
X	EP 0 458 743 A (CIBA GEIGY AG) 27 November 1991 (1991-11-27)	1-4,15, 16,25-28
Y	page 51, lines 1-10; page 14, lines 1-9; claims 1-8,13,14,17-22	1-30
Y	EP 0 625 551 A (CIBA GEIGY AG) 23 November 1994 (1994-11-23) cited in the application claims 1-7,17,18	1-30
	---	-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

3 November 1999

Date of mailing of the international search report

18/11/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Ginoux, C

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02447

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 20 01 960 A (IMPERIAL CHEMICAL INDUSTRIES LIMITED ) 30 July 1970 (1970-07-30) claims & GB 1 283 771 A cited in the application -----	1-30
A	EP 0 818 513 A (ZENECA LTD) 14 January 1998 (1998-01-14) claims 1-5,7-9 -----	1-30
A	PATENT ABSTRACTS OF JAPAN vol. 012, no. 015 (C-469), 16 January 1988 (1988-01-16) & JP 62 172062 A (MITSUBISHI CHEM IND LTD), 29 July 1987 (1987-07-29) cited in the application abstract -----	1-30

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/GB 99/02447

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9318224 A	16-09-1993	AU 677575 B		01-05-1997
		BR 9306026 A		18-11-1997
		CA 2129750 A		07-09-1993
		DE 69307301 D		20-02-1997
		DE 69307301 T		15-05-1997
		DK 629249 T		27-01-1997
		EP 0629249 A		21-12-1994
		ES 2098727 T		01-05-1997
		HK 1004573 A		27-11-1998
		JP 7504949 T		01-06-1995
		US 5525124 A		11-06-1996
EP 0458743 A	27-11-1991	JP 4227970 A		18-08-1992
EP 0625551 A	23-11-1994	CN 1104661 A		05-07-1995
		JP 6329941 A		29-11-1994
DE 2001960 A	30-07-1970	CH 541610 A		31-10-1973
		CH 541611 A		31-10-1973
		CH 542268 A		15-11-1973
		CS 178065 B		31-08-1977
		CS 178098 B		31-08-1977
		CS 178099 B		31-08-1977
		ES 375496 A		16-05-1972
		ES 378464 A		16-06-1972
		ES 378465 A		16-06-1972
		FR 2028479 A		09-10-1970
		GB 1283771 A		02-08-1972
		NL 7000663 A,B		20-07-1970
		US 3647778 A		07-03-1972
EP 0818513 A	14-01-1998	NONE		
JP 62172062 A	29-07-1987	JP 1933608 C		26-05-1995
		JP 6062873 B		17-08-1994